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COMPLETE SPECIFICATION

Improvements in or relating to Articles

We, DUNLOP RUBBER COMPANY LIMITED, a British Company of 1, Albany Street, London, N.W.1. do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to polyurethane covered golf-balls.

Articles are conveniently coated with polyurethane by applying a liquid polyurethane prepolymer to the surface thereof. However, when these articles have interstices in their surfaces the liquid polyurethane prepolymer penetrates the surface of the article and may trap air in the body of the article, which air may escape and cause defects, namely air bubbles, in the polyurethane layer when heat is applied to cure the prepolymer. This is particularly true in the instance of polyurethane covered golf-balls in which a rubber-thread wound golf-ball core is coated with a polyurethane prepolymer since the prepolymer penetrates into the interstices of the thread wound core and traps air which migrates into the polyurethane layer causing defects namely air bubbles in the layer when the prepolymer is cured. If the polyurethane has been applied to the core in a mould under pressure, the pressure of the air sealed into the core may be substantially greater than atmospheric pressure. When heat is applied to cure the polyurethane prepolymer, the air under pressure may blow out into the polyurethane layer. The Applicants have discovered that the egress of air may be overcome by accelerated curing of the polyurethane in the layer immediately adjacent the surface being coated without loss of adhesion between the surface and the polyurethane.

The present invention therefore provides a golf-ball having a core and a layer of poly-

urethane coated on the surface of said core, wherein there has been accelerated curing of the polyurethane in said layer immediately adjacent said surface.

The present invention further provides a method of coating the surface of a golf-ball core with a layer of polyurethane comprising forming a layer of an accelerating curing agent on said surface, applying polyurethane on the layer of accelerating curing agent and curing the polyurethane, wherein the polyurethane immediately adjacent said surface is subjected to an accelerated cure.

In the method of the present invention the polyurethane immediately adjacent the surface being coated is subjected to an accelerated cure at just below the interface of the accelerated curing agent and the polyurethane to form an air-impervious skin which prevents migration of air from the core into the polyurethane layer. In effect in the initial stages of curing the polyurethane layer, the polyurethane and accelerator react to form the air-impervious skin while the remainder of the polyurethane in the layer cures at a much slower rate. Suitably the agent which is employed to effect accelerated curing is a compound containing at least two isocyanate-reactive groups per molecule other than a diol or aromatic amine and is preferably a primary aliphatic polyamine such as tetraethylene pentamine, ethylene diamine, propylene diamine or a primary-amine-group-containing polyamide such as those commercially available under the names Versamids 100, 120 and 125 and Beckalides 189 and 193. Versamid is a Registered Trade Mark. Preferably the polyamine is a viscous fluid since a low viscosity liquid polyamine would tend to be displaced by the polyurethane layer formed in it. However, mobile polyamines may be employed by thickening them to a

suitable viscosity. A suitable thickener is commercially available under the name Visco 699.

5 It will be understood of course that the polyurethane applied to the surface of the core will normally contain a conventional cross-linking or curing agent such as a diol or feebly basic polyamine e.g. an aromatic polyamine, these compounds curing the polyurethane at a comparatively slow rate.

10 For the sake of brevity the agent employed to effect accelerated curing will be referred to hereafter as "accelerator", and the word "accelerator" is hereafter to be understood to mean the accelerating curing agent.

15 The coated surface according to the present invention is made by first coating the surface of the core with the accelerator. This may conveniently be achieved by employing a solution of the accelerator in a suitable solvent, the solution being sprayed or brushed onto the surface or alternatively the surface is immersed in the accelerator solution. The choice of solvent is important since it is necessary to choose a solvent which does not have a deleterious effect on the surface being coated. Thus if a rubber surface is being coated the solvent should not have a swelling effect on the rubber and in practice the lower aliphatic alcohols such as methanol, ethanol and propanol would be employed. The solvent is conveniently removed from the accelerator by heat. The concentration of the accelerator in the solution may vary over a wide range but normally a solution containing from 10 to 50% of accelerator will be employed.

35 The amount of accelerator deposited upon the surface of the core may be controlled by adjusting the concentration of the accelerator in the solvent and the technique by which the accelerator is applied.

40 The polyurethane prepolymer may be applied to the accelerator-coated surface by various methods including injection moulding, applying a pre-formed partially cured polyurethane prepolymer or merely forming a polyurethane layer on the accelerator-coated surface.

45 After the polyurethane prepolymer is applied it is then cured to cross-link the polyurethane prepolymer to a more solid mass. The curing is conveniently carried out by heating the coated article.

50 The term "polyurethane prepolymer" is used herein for convenience to distinguish the starting material from the cured polyurethane in the final golf-ball cover. However, it will be understood that the polyurethane prepolymer is itself a polymer and not merely an intermediate therefor. The polyurethane prepolymer may be a viscous liquid or an elastomeric material. In general we prefer for convenience in handling to use liquid prepolymers. The production of polyurethane-

prepolymers is well known. Generally, they are prepared by reacting an organic polymer containing hydroxyl groups with an organic polyisocyanate or polyisothiocyanate. Examples of such organic polymers include polyesters, polyethers, and polyesteramides, all of which must, however, contain residual isocyanate-reactive groups. Examples of suitable polyesters include polyethylene glycol adipate and also copolyesters. Examples of suitable polyethers include polyglycols from propylene oxide and tetrahydrofuran. The process according to the invention is particularly suited to polyethers prepared from tetrahydrofuran but is not limited thereto. Polyisocyanates which may be used include naphthalene diisocyanate, tolylene diisocyanate and diphenyl methane diisocyanate. Polyurethane prepolymers which may be used include Adiprene L 167, a commercially available prepolymer prepared from polytetrahydrofuran and tolylene diisocyanate.

As previously stated curing of the bulk of the polyurethane is preferably effected by means of a conventional curing agent e.g. diols, feebly basic diamines, etc., but water is preferably not used as a cross-linking agent since, as is known, it reacts with isocyanate end-groups to evolve carbon dioxide; this is undesirable if a good finish is to be obtained on a finished golf-ball.

The polyurethane prepolymer-cross-linking agent mixture may be used alone or may be admixed with other materials, for example, mineral oils, fillers and colouring materials.

In the normal manufacture of golf-balls according to the present invention, the rubber-thread wound core is preferably protected from unwinding by placing a few isolated spots of adhesive such as a polyurethane prepolymer on the tucked-under end of the thread.

The polyamide resin is then coated onto the core preferably by dipping the core into a bath or other vessel containing a dilute solution containing from 10 to 50% particularly from 20 to 30% of a polyamide resin in methanol. The solvent is then driven off by heating the core at a suitable temperature.

The polyamide-resin-coated core is then coated with a polyurethane prepolymer preferably by placing the core in an injection mould maintained at an elevated temperature (suitably 70° to 110°C.) and the prepolymer containing a cross-linking agent is injected into the mould. The mould is then placed in an oven maintained at an elevated temperature to cure the polyurethane prepolymer. The ball is then separated from the mould and given a final press-cure at an elevated temperature in a conventional golf-ball mould which imprints the pattern and lettering if desired.

The polyurethane prepolymer may also be applied to the polyamide-resin-coated core by

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supporting the core by pins or other means and applying a layer of polyurethane prepolymer to the surface of the core while it is being coated. The coated ball is then maintained at an elevated temperature to effect curing of the prepolymer and then cooled. The polyurethane-coated ball is then finally press-cured as before.

In our copending Application No. 990784 there are described two methods such as those above which are particularly useful for the application of the polyurethane prepolymer to the polyamide-resin-coated golf-ball core.

A further method by which the polyurethane prepolymer may be applied is by forming two half shells of a partially cured polyurethane prepolymer, placing these around the polyamide resin treated core, and then placing the assembled ball in a patterned mould and heating it. Such a method is described in our copending Application No. 968,987.

The manufacture of golf-balls according to the present invention is illustrated in the following example.

EXAMPLE.

A golf-ball core was protected against unwinding by placing on it six evenly spaced spots of a polyurethane composition, including a spot on the tucked-under end thread. The polyurethane composition was composed of 100 parts of Adiprene L 167 (a liquid prepolymer of polytetrahydrofuran and tolylene diisocyanate) and 20 parts of methylene bis (orthochlor-aniline) as a cross-linking agent. (Methylene bis(orthochloraniline) is hereafter abbreviated to "MOCA").

The following day the core was immersed for 3 seconds in a bath containing 1 part by weight of Versamid 125 and 3 parts by weight of methanol and the solvent was removed by placing the core in an air oven maintained at 40°C. The following day the treated core was placed in the cavity between two injection mould halves, the inner dimensions of the halves when together having approximately the external dimensions of a golf-ball. The mould halves had sufficient supports to locate the core centrally in the mould.

A polyurethane composition was prepared from 100 parts by weight of Adiprene L 167, 20 parts of MOCA and 10 parts of titanium dioxide as follows:— the titanium dioxide was dried by heating and allowed to cool in a closed container. The titanium dioxide was then mixed with the MOCA and the mixture ball milled to break down aggregates of titanium dioxide. The mixture of titanium dioxide and MOCA was transferred to a vessel which was evacuated and heated to 140°C. The MOCA was melted and dissolved gas was removed. The vacuum was released and the mixture stored in an oven at

110°C. in a sealed container. Prior to use the mixture was agitated.

The prepared titanium dioxide/MOCA mixture at 110°C. was added to the Adiprene L 167 maintained at room temperature in a stainless steel container and the mixture vigorously stirred. Exposure of the Adiprene L 167 to the atmosphere was kept to a minimum to avoid reaction with atmospheric moisture. The mixture was kept under vacuum for two minutes to eliminate dissolved gas.

The stainless steel container was connected to the injection mould by means of an injection tube which led from below the surface of the Adiprene L 167/titanium dioxide/MOCA mixture up to the injection port of the mould which was positioned above the container. The whole assembly was maintained at 80°C. Dried compressed air at 10 p.s.i. was then admitted into the container thus forcing the polyurethane prepolymer-containing composition in the container up the injection tube into the injection mould cavity until the polyurethane prepolymer-containing composition appeared in the spew-port located at the top of the injection mould. At this point the spew-port was sealed and the pressure raised to 30 p.s.i.

The whole apparatus was then placed in an oven at 80°C. for 8½ minutes. It was subsequently withdrawn and the mould assembly cooled to 10°C. and opened. The resultant preformed ball was entirely bubble-free. A number of experiments in which this technique was employed all resulted in bubble-free products.

The preformed ball, from which "sprues" has been removed, was then given a final press-cure of 10 minutes at 100°C. in a conventional golf-ball mould which imprinted the lettering and pattern.

The complete ball was entirely bubble-free, showed no signs of support marks or excrescences. Tests showed that it had a superior cutting resistance to that of the standard gutta-percha-covered ball and from inspection of the ball after it had been cut into two pieces it was observed that the polyurethane cover had adequately adhered to the core of the ball.

WHAT WE CLAIM IS:—

1. A golf-ball having a core and a layer of polyurethane coated on the surface of said core, wherein there has been accelerated curing of the polyurethane in said layer immediately adjacent said surface.
2. A golf-ball according to claim 1, wherein the curing of the polyurethane in said layer immediately adjacent said surface has been accelerated by a compound containing at least two isocyanate-reactive groups per molecule, not being a diol or an aromatic amine.

3. A golf-ball according to claim 2, wherein said curing has been accelerated by a primary aliphatic polyamine.
- 5 4. A golf-ball according to claim 2, wherein said curing has been accelerated by a primary-amine-group-containing polyamide.
- 10 5. A golf-ball according to any of the preceding claims wherein the layer of polyurethane has been formed from a polyurethane prepolymer prepared from polytetrahydrofuran and tolylene diisocyanate.
- 15 6. A method of coating the surface of a golf-ball core with a layer of polyurethane comprising forming a layer of an accelerating curing agent on said surface applying polyurethane on the layer of accelerating curing agent and curing the polyurethane wherein the polyurethane immediately adjacent said surface is subjected to an accelerated cure.
- 20 7. A method according to claim 6, wherein the accelerating curing agent is applied to the surface to be coated in a solution containing 10% to 50% of the accelerating curing agent.
- 25 8. A method according to either of claims 6 and 7, wherein the accelerating curing agent employed is a compound containing at least two isocyanate-reactive groups per molecule, not being a diol or an aromatic amine.
9. A method according to claim 8, wherein the accelerating curing agent is a primary aliphatic polyamine. 30
10. A method according to claim 8, wherein the accelerating curing agent is a primary-amine-group-containing polyamide. 35
11. A method according to claim 10, wherein the polyamide is applied to the surface of the golf-ball core by dipping the core into a solution containing from 20% to 30% of polyamide resin in methanol. 40
12. A method according to claim 11, wherein the core after being dipped in polyamide resin solution is then coated with polyurethane prepolymer in an injection mould. 45
13. A method according to any of the claims 6 to 12, wherein the layer of polyurethane is formed from a polyurethane prepolymer prepared from polytetrahydrofuran and tolylene diisocyanate.
14. A method of coating a golf-ball core substantially as described in the example above. 50
15. A golf-ball produced by a method substantially according to any of the claims 6 to 14 above. 55

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